Saskatchewan
Research Council

ATOMIC ABSORPTION METHOD FOR QUANTITATIVE DETERMINATION OF CARBONATES IN TILLS

by

W.C. Ross

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INTRODUCTION

Previously, carbonate analysis of tills by the Saskatchewan Research Council was done by using a gasometer technique and equipment as described by Christansen and Ross (1971), Perkins and Dyck (1973) and Ross (1986). More recently the Atomic Absorption analytical method (AA) is being used for carbonate analyses of tills. The following is an explanation of this method and a comparison of the results between the gasometer and atomic absorption methods.

DESCRIPTION OF THE SPECTROPHOTOMETER

The components of the spectrophotometer, their operational functions and maintenance, are described in the manufacturer's instrument manual. A copy is in reserve in the laboratory reference library of the Saskatchewan Research Council.

LABORATORY OPERATIONS

Laboratory procedures are described in detail in the Appendix of this report.

Appendices: 2A – Sample Preparation

2B – Reagents

2C – Procedure for Extraction

2D – Procedure for Interfiring Ion Supression, Dilution, and Buffer

2E – Procedure for Spectrophotometer Operation

2F – Manual Calculations

2G – Computer Calculations.

LIMITATIONS

The Atomic Absorption Method of carbonate analyses is designed to measure calcium and magnesium ions in the filtrate of acid–leached samples. These ions are derived from the carbonate minerals of calcite and dolomite, and from any other acid soluble salts which may be present in the sample.

In the analyses of glacial tills, the samples are recovered from the parent materials and they are usually void of other calcium–magnesium minerals. However, in the case of buried land surfaces, the samples may contain minute grains of gypsum, and other acid soluble salts which may escape visual detection. If such minerals are suspected to be present then positive identification of calcium–magnesium minerals, other than calcite and magnesium, is required, either by microscopic examination, or X–ray diffraction in order to give a proper account of the total calcium and magnesium.

RESULTS OF THE ATOMIC ABSORPTION METHOD COMPARED TO THE GASOMETER METHOD

Results of analyses are considered to be absolute when compared to the results from Gasometer analyses. Identical samples were split in half. Each half was analyzed by the two methods, and the statistical evaluation of the results by linear regression revealed both methods to be comparable.

Table I contains the analytical results of the duplicate analyses, and the linear regression curves are illustrated by Figure I, 2, 3. The statistical parameters are as follows:

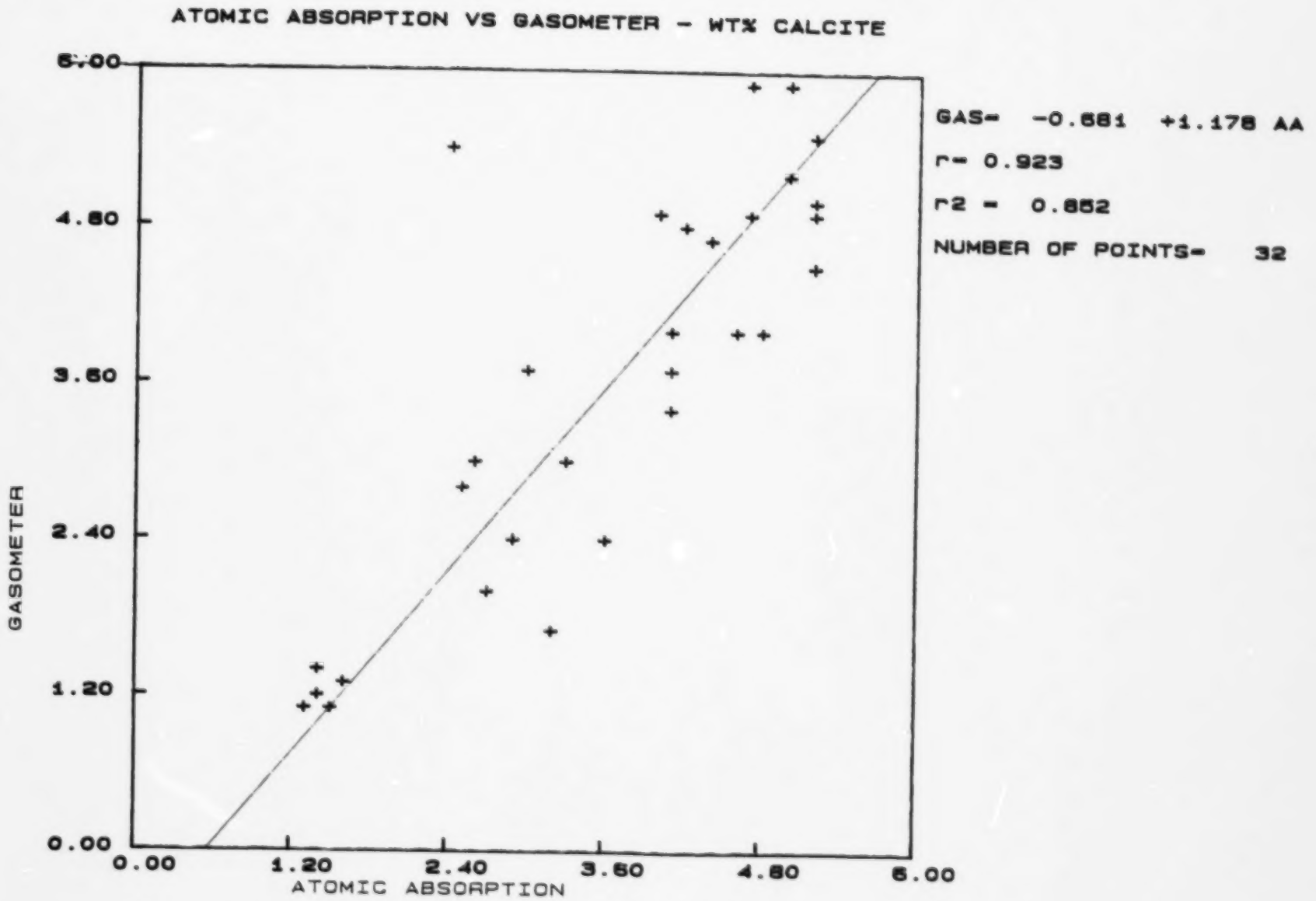

Figure 1 - Linear Regression for Weight Percent Calcite.

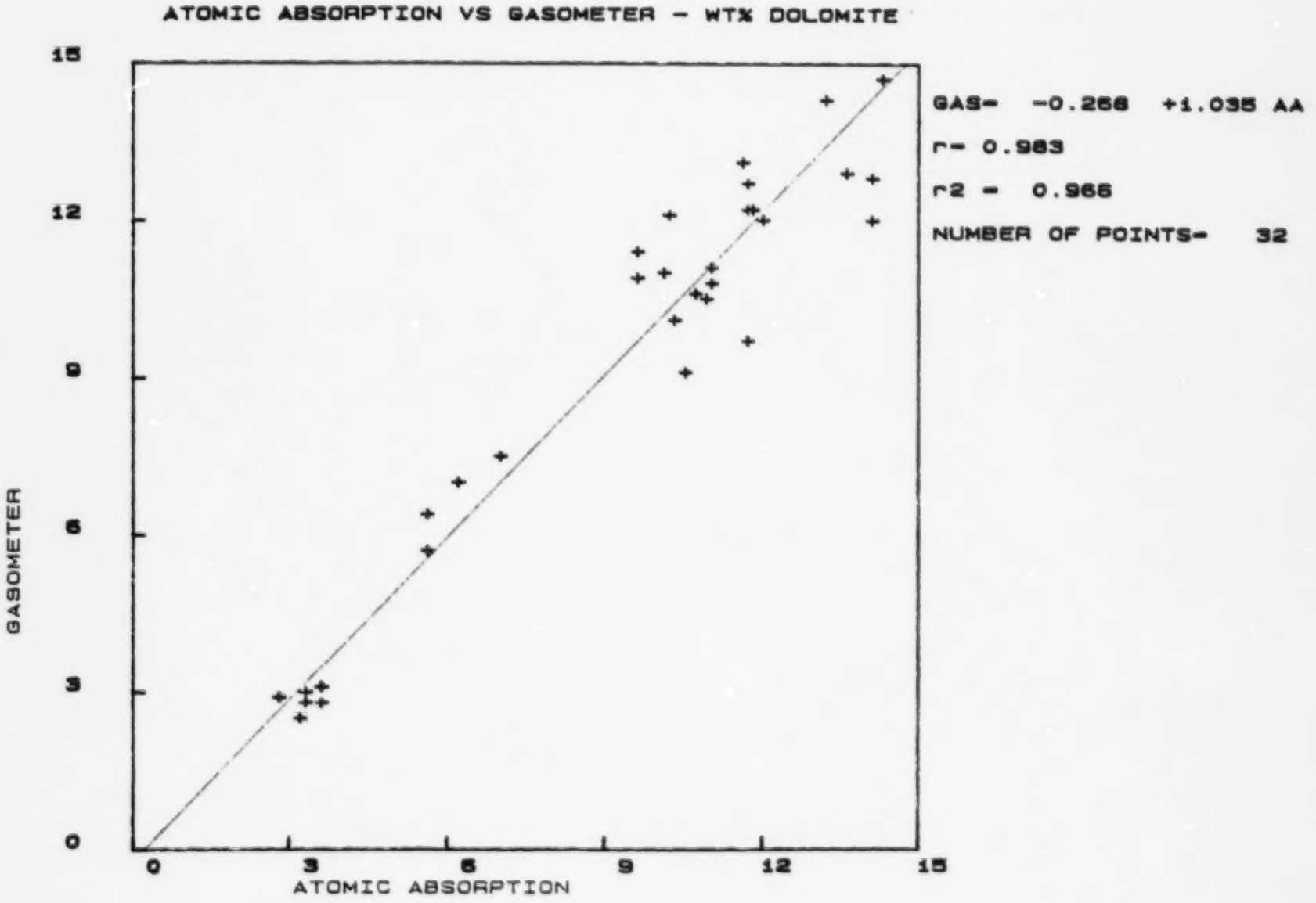

Figure 2 - Linear Regression for Weight Percent Dolomite.

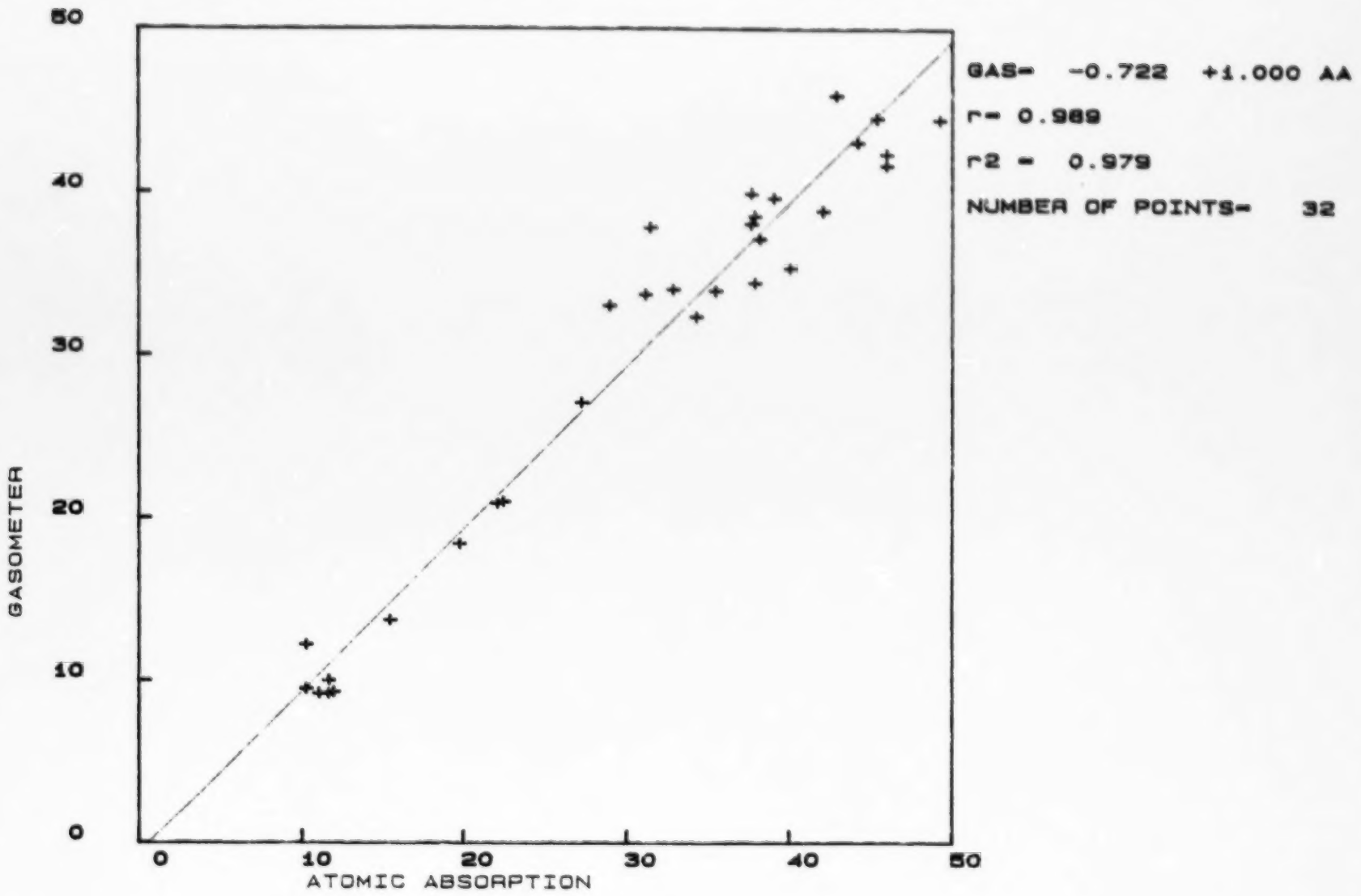

Figure 3 - Linear Regression for Total CO_2 Evolved: $m/s_{/gm}$

Table 1. Comparative Analyses; Results used in Linear Regression Evaluation

Sample Name	Depth(ft)	Weight% Calcite AA.	Calcite Gas	Weight% Dolomite AA	Dolomite Gas	Total CO_2 AA.	(m/s/gm) Gas
Dalmeny SE1–13:	10	2.6	3.0	9.6	10.9	28.9	33.0
	15	2.9	2.4	9.6	11.4	35.4	33.9
	20	4.1	3.4	10.3	10.1	34.2	32.3
	30	3.0	3.7	10.7	10.6	32.8	34.0
	45	2.5	2.8	10.1	11.0	31.1	33.7
	55	4.1	3.7	11.7	12.1	37.6	38.0
	60	4.1	4.0	11.7	12.7	37.6	39.9
	65	4.1	4.0	11.8	12.2	37.8	38.5
Sutherland SW12–1	25	4.8	4.0	14.3	14.7	45.3	41.5
	30	5.0	5.2	13.6	12.9	44.1	43.0
	40	4.2	4.8	11.7	9.7	37.8	34.4
	70	4.7	4.9	11.6	13.1	42.8	45.9
	80	5.2	5.5	14.1	12.0	45.9	41.6
	80–rerun	5.2	5.0	14.1	12.8	45.9	42.3
	90	5.2	4.5	13.2	14.3	49.2	44.4
	140	2.7	2.0	5.6	5.7	19.7	18.4
	150	3.2	1.7	6.2	7.0	22.4	21.0
	170	4.6	4.0	7.0	7.5	27.2	27.1
	180	3.6	2.4	5.6	6.4	22.0	20.9
	200	3.3	3.0	3.3	3.0	15.4	13.7
	215	1.4	1.2	3.6	3.1	11.9	9.3
	240	1.6	1.3	3.3	2.8	11.6	10.0
	250	1.5	1.1	2.8	2.9	10.2	9.5
	270	1.3	1.1	3.6	2.8	11.6	9.2
	290	1.4	1.4	3.2	2.5	11.0	9.2
T4	10	4.0	4.9	10.2	12.1	10.2	12.2
	15	2.4	5.4	10.7	10.6	31.4	37.8
	20	4.4	4.7	12.0	12.0	39.0	39.6
	25	4.7	5.9	10.9	10.5	42.0	38.8
	30	5.2	4.9	11.0	10.8	38.1	37.1
	35	5.0	5.9	10.5	9.1	40.0	35.3
	30–rerun	5.2	4.5	11.0	11.1	38.1	37.1

(1) calcite, – coefficient of correlation is 0.923

(2) dolomite, – coefficient of correlation is 0.983

(3) Total CO_2 evolved – coefficient of correlation is 0.989

PRECISION

Table 2 shows the precision to be satisfactory. Based on 30 analyses the results are as follows:

Calcite – standard deviation is 0.51 for mean value = 4.48

Dolomite – standard deviation is 0.55 for mean value = 10.96

Total CO_2 evolved – standard deviation is 1.62 for mean value = 36.7

ERROR

The precision (reproducibility) of the results has proved to be acceptable; however, there is a slight variation between the results of duplicate analyses (assuming no human error).

The variation is attributed to one or more of the potential factor which are as follows:

1) Inhomogeneity of carbonate distribution within a sample due to insufficient mixing
2) Incomplete extraction of the carbonates in the preparation of the filtrate for Atomic Absorption Analyses
3) A degeneration of the chemicals with time which are used as buffers to suppress specific ions

RECORD OF THE ANALYTICAL RESULTS

Table 2. Results of the Atomic Absorption Spectrophotometric Method for Quantitative Carbonate Analyses

Sample Name	Calcite wt.%	Dolomite wt.%	Total CO_2 m/s/gm	Sample Name	Calcite wt.%	Dolomite wt.%	Total CO_2 m/s/gm
T1	4.56	10.5	35.4	T16	4.13	10.6	35.0
T2	4.29	10.5	35.0	T17	5.68	11.1	39.6
T3	4.75	11.1	37.5	T18	4.34	11.4	37.4
T4	4.21	11.1	36.5	T19	4.92	10.4	36.3
T5	4.76	11.1	37.7	T20	4.39	12.1	39.1
T6	4.14	12.3	39.1	T21	4.21	10.7	35.4
T7	4.00	10.6	35.2	T22	3.89	11.6	36.9
T8	4.36	10.9	36.3	T23	5.19	11.2	38.9
T9	4.44	10.5	35.6	T24	3.77	11.7	36.8
T10	4.00	10.2	33.8	T25	3.88	10.8	35.0
T11	4.07	10.8	35.3	T26	4.22	10.6	35.3
T12	4.88	11.1	37.8	T27	4.40	10.2	34.7
T13	4.02	10.8	35.2	T28	5.52	10.4	37.6
T14	5.37	11.2	39.7	T29	4.21	11.8	38.0
T15	4.36	11.6	38.0	T30	5.22	10.4	36.9

Sample BTS 10002 depth 42 ft.

Sample Treatment:

<2 mm grain size fraction
oven–dried 5 hrs. at 105°C

carbonate extraction by 20 hr. leaching with std. volume of 1:1 HCl

The Atomic Absorption Spectrophometer is connected directly to a pre–programmed computer. The printer component prints out, in orderly fashion, the required information. Table 3 illustrates the record sheet of the analyses of 38 samples from a testhole.

This record is complete containing all pertinent data of the analyses. Storage of this analytical record is kept within the testhole file with other types of analyses such as grain size distribution.

CONCLUSIONS

The results of carbonate analyses by the Atomic Absorption Method are comparable to those analysed by the Heinze Gasometer Method. The slight variations in reproducability do not effect the values of the parameters appreciably and are within acceptable limits to be applied to the studies of glacial till.

The Atomic Absorption Method is advised for the anlayses of large numbers of samples. Sample preparation is similar, however, the cost per analyses is less than the analysis by gasometer.

The advantages of the Gasometer Method are that the equipment is small and portable, and the initial equipment cost is about 1/5 that of the A.A. Spectrophotometer.

R89 MCKNIGHT SRC DEC.8/87 (58) PGS.835,836 [CA MG DIG.]

1 %CA BY AA
2 %MG BY AA
3 WT% DOLOMITE=COL.2*7.5852
4 WT% CA IN DOLOMITE=COL.3*1.8485
5 WT% CA IN CALCITE=COL.1-COL.4
6 WT% CALCITE=COL.5*2.4973
7 CO2 FROM CALCITE=COL.6*2.238
8 CO2 FROM DOLOMITE=COL.3*2.429
9 TOTAL CO2=COL.7+COL.8

	CA	MG	WT%DO	W%CADOW%CACAL	WT%CAL	CO2CAL	CO2DOL	CO2TOT
BR1	4.77	1.57	11.91	2.59 2.18	5.45	12.19	28.93	41.12
WAW 6	3.84	1.62	12.29	2.67 1.17	2.92	6.53	29.85	36.38
WAW 10	3.23	1.31	9.94	2.16 1.07	2.67	5.98	24.14	30.12
WAW 13	2.87	1.13	8.57	1.86 1.01	2.51	5.63	20.82	26.45
WAW 16	3.00	1.19	9.03	1.96 1.04	2.59	5.80	21.93	27.73
WAW 30	3.69	1.22	9.25	2.01 1.68	4.19	9.38	22.48	31.86
WAW 33	4.37	1.36	10.32	2.24 2.13	5.31	11.89	25.06	36.95
WAW 36	3.64	1.11	8.42	1.83 1.81	4.52	10.12	20.45	30.57
WAW 80	3.08	1.11	8.42	1.88 1.20	3.00	6.71	20.45	27.16
WAW 83	3.28	1.11	8.42	1.88 1.45	3.62	8.10	20.45	28.56
WAW 86	4.21	1.24	9.41	2.04 2.17	5.41	12.10	22.85	34.95
WAW 90	3.91	1.02	7.74	1.68 2.23	5.57	12.45	18.79	31.25
WAW 93	3.49	0.98	7.43	1.62 1.87	4.68	10.48	18.06	28.53
WAW 96	3.59	1.04	7.89	1.71 1.88	4.68	10.48	19.16	29.64
WAW 100	3.56	1.01	7.66	1.67 1.89	4.72	10.59	18.61	29.20
WAW 103	3.37	0.89	6.80	1.37 2.20	5.50	12.30	15.39	27.69
WAW 106	3.48	0.80	6.07	1.32 2.11	5.27	11.80	14.74	26.54
WAW 110	3.43	0.90	6.83	1.48 1.95	4.86	10.88	16.58	27.46
WAW 113	2.99	0.80	6.07	1.32 1.67	4.17	9.34	14.74	24.08
WAW 116	3.48	1.05	7.96	1.73 1.75	4.37	9.77	19.35	29.12
BR1	4.80	1.58	11.98	2.60 2.20	5.49	12.27	29.11	41.38
WAW 120	3.24	0.82	6.22	1.35 1.72	4.30	9.63	15.95	25.58
WAW 123	3.17	0.79	5.99	1.30 1.87	4.66	10.44	14.56	24.99
WAW 126	3.12	0.88	6.67	1.45 1.67	4.17	9.33	16.21	25.54
WAW 130	2.45	0.68	5.16	1.12 1.33	3.32	7.43	12.53	19.96
WAW 133	3.23	0.75	5.69	1.24 1.99	4.98	11.14	13.82	24.96
WAW 136	2.58	0.72	5.46	1.19 1.87	4.68	10.47	13.27	23.74
WAW 140	1.48	0.83	6.29	1.37 1.44	3.59	8.04	15.42	23.46
WAW 143	3.16	0.71	5.38	1.17 1.88	4.72	10.56	13.05	23.61
WAW 146	2.59	0.68	5.16	1.12 1.47	3.67	8.21	12.53	20.74
WAW 150	3.16	0.66	5.01	1.09 2.07	5.17	11.58	12.16	23.74
WAW 153	2.60	0.65	4.93	1.07 1.53	3.82	8.54	11.98	20.52
WAW 156	2.88	0.87	6.60	1.43 1.38	3.44	7.71	16.04	23.75
WAW 161	2.87	0.79	5.99	1.30 1.42	3.54	7.93	14.56	22.49
WAW 166	2.95	0.82	6.22	1.35 1.60	3.99	8.93	15.11	24.04
WAW 170	2.36	0.56	4.25	0.92 1.44	3.59	8.03	10.32	18.35
WAW 173	2.53	0.75	5.69	1.24 1.29	3.23	7.23	13.82	21.05
WAW 176	2.78	0.71	5.38	1.17 1.52	3.84	8.58	13.08	21.66
WAW 180	2.41	0.58	4.39	0.96 1.48	3.71	8.31	10.66	18.97

Table 3. Record sheet of analyses of 38 samples.

REFERENCES

Christiansen, E.A., and Ross, W.C., 1971. Carbonate analysis of tills using a continuously recording gasometer. Saskatchewan Research Council Circular 5–G71–5, 12 p.

Perkins, E.H. , and Dyck J.H., 1973. Heinze Gas–volugraph, Saskatchewan Research Council Report p.73–6, 89p.

Ross, W.C., 1986. Heinze gasometer method for quantitative determination of carbonates in tills. Saskatchewan Research Council Technical Report No. 215, 38 p.

APPENDIX 1

LABORATORY PROCEDURES FOR CARBONATE ANALYSES BY THE ATOMIC ABSORPTION METHOD

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LABORATORY PROCEDURES FOR CARBONATE ANALYSES BY THE ATOMIC ABSORPTION METHOD

1A – Sample Preparation

1B – Reagents

1C – Procedure for Extraction

1D – Procedure for Interfering Ion Suppression, Dilution, and Buffer

1E – Procedure for Spectrophotometer Operation

1F – Manual Calculations

1G – Computer Calculations

1A – Sample Preparation

(1) Oven dry samples for 5 hours at a controlled temperature of 105°C, then cool in a desiccator.

(2) Reduce clods, or aggregates, with a wooden rolling pin on a wooden board.

(3) Sieve each sample through a 2 mm screen. Pebbles caught on screen are discarded, or bottled and labelled for future mineralogic studies.

(4) Transfer minus 2 mm screenings into a pre–labelled glass bottle and reheat in drying oven at 105°C for 1 1/2 hours.

(5) Cool in desiccator.

(6) Cap bottled samples and place in reserve for carbonate analyses by the Atomic Absorption Method.

1B – Reagents

(required for AAS analyses)

(1) Lanthanum – concentration 50,000 g/l

Preparation is as follows:

Wet 58.64 gm of lanthanum oxide, La_2O_3, with 50 ml deionized water. Slowly and cautiously add 250 ml of concentrated HCl to dissolve the La_2O_3. Dilute to 1 litre with deionized water.

Note: Silicon, aluminum, phosphate, and sulphate depress the sensitivity for calcium. It is known that calcium sensitivity is depressed by titanium and zirconium. Lanthanum or strontium at concentrations of 0.1 to 1% can be added to the samples and standards to control these

interferences, and simultaneously a slight ionization interference for calcium in the air–acetylene flame. Acid concentrations of the standards should be matched with that of the sample.

(2) Standard Solutions of Carbonates

(For Atomic Absorption Spectrophotometer adjustments)

Standard solutions are purchased from Fisher Scientific and certified as follows:

Calcium – 5 ppm calcium standard – 0.94% calcium by weight
– 15 ppm calcium standard – 2.83% calcium by weight
– 30 ppm calcium standard – 5.65% calcium by weight

magnesium – 5 ppm magnesium standard – 0.94% magnesium by weight
– 10 ppm magnesium standard – 2.83% magnesium by weight
– 30 ppm magnesium standard – 5.65% magnesium by weight

(3) Deionized Water

(4) 1:1 HCl acid

1C – Procedure for Extraction

(Free carbonates from sample by acid leaching)

(1) Weigh 1.000 ± .002 gm of moisture–free sample passed through 2.0 mm mesh sieve into a 40 ml pyrex test tube.

(2) Add 20.00 ± .002 ml of 1:1 HCl acid from a repipette.

(3) Stopper test tube and shake. Allow to stand for 24 hours.

(4) Stopper and reshake, then withdraw 50 ± 2 l (50 microlitres) with micropipette and add to precleaned 40 ml pyrex test tube.

(5) Withdraw 50 l of deionized water with micropipette (cleaning operation) and add to the 50 l extract in 40 ml test tube (to above operation 4).

1D – Procedure for Interfering Ion Suppression, Dilution, and Buffer[1]

The automatic diluter is pre–adjusted to dispense the necessary volume of lanthum to suppress interfering ions, the proper dilution and acidity to match the required operational range of the Atomic Absorption Spectrophotometer.

(1) The automatic diluter is engaged to add 3.69 ml of deionized water plus 0.92 ml of lanthanum (5% by weight) to the sample extract (total volume is 4.71 ml).

Note: The dilution factor is 1884, and is determined as follows:

$$\text{dilution} - \frac{\text{total volume}}{\text{sample volume}} = \frac{4.71}{.05} = 94.2$$

with 1 gm of sample in 20 ml of 1:1 HCl

total dilution factor = 94.2 x 20

= 1884

[1] Procedure for —— buffer – this efficient operation was designed and is used by Mr. Al Holsten, Geochemistry Laboratory of Saskatchewan Research Council.

1E – Procedure for Spectrophotometer Operation

(1) Turn on Spectrophotometer and recorder.

(2) Analyse standard samples of calcium and magnesium. Make necessary adjustments so that Spectrophotometer reads absolute weight percentages of calcium and magnesium.

(3) Proceed to analyse unknown samples. The print–out gives sample number, weight percentages of calcium and magnesium.

Note: When analysing a large number of samples it is advisable to check the absolute values of calcium and magnesium against standards about every tenth analyses, and make required adjustments to Spectrophotometer when necessary.

1F – Manual Calculations

Note: Calculations convert the weight percentages of calcium and magnesium, which are read from the print–out of the Atomic Absorption Spectrophotometer, to weight percentages of calcite and dolomite and their CO_2 volume equivalent, at standard temperature and pressure.

The general formulae, listed below, employ stoicheometric relationships of the chemical reactions.

Actual values of weight percentages of calcium and magnesium can be substituted in the equations, as follows:

(1) Wt% dolomite

$$= \text{wt\% magnesium} \times \frac{\text{GMW dolomite}}{\text{GMW magnesium}}$$

$$= \text{wt\% magnesium} \times \frac{184.412}{24.312}$$

$$= \text{wt\% magnesium} \times 7.5852$$

(2) Wt% calcium in dolomite

$$= \text{wt\% magnesium} \times \frac{\text{GMW calcium}}{\text{GMW magnesium}}$$

$$= \text{wt\% magnesium} \times \frac{40.08}{24.312}$$

$$= \text{wt\% magnesium} \times 1.6486$$

(3) Wt% calcium in calcite

= wt% calcium in sample – wt% calcium in dolomite

(4) Wt% calcite

$$= \text{wt\% calcium in calcite} \times \frac{\text{GMW calcite}}{\text{GMW calcium}}$$

$$= \text{wt\% calcium in calcite} \times \frac{100.09}{40.08}$$

$$= \text{wt\% calcium in calcite} \times 2.4973$$

(5) Total CO_2 Equivalent/gm of Sample

(= CO_2 evolved by calcite + CO_2 evolved by dolomite/gm of sample)

(a) CO_2 evolved by calcite/gm of sample

$$= \frac{\text{wt\% calcite} \times 22{,}400}{100 \times 100.09}$$

= wt% calcite x 2.238 (mls/gm of sample)

(b) CO_2 evolved by dolomite/gm of sample

$$= \frac{\text{wt\% dolomite} \times 22{,}400}{100 \times 92.206^{3}}$$

= wt% dolomite x 2.429 (mls/gm of sample)

Total CO_2 equivalent/gm of sample

= (a) + (b)

1G – Computer Calculations

The calculations of a large number of carbonate analyses may be more efficiently done by a programmed basic computer.

The program employed is as follows:

CARBS

```
10  PRINT "WHEN FINISHED TYPE DONE FOR SAMPLE NAME"
20  PRINT "Enter the sample name";
25  DIM S$[20]
30  INPUT S$
40  IF S$="DONE" THEN 190
41  PRINT "ENTER A (WT % CALCIUM)"
42  INPUT A
50  PRINT "ENTER B (WT % MAGNESIUM)"
70  INPUT B
80  C=B*7.5852
90  D=B*1.6486
100 E=A-D
110 F=E*2.4973
120 G=(F/100)*(22400/100.09)
130 H=(C/100)*(22400/92.205)
140 PRINT "CALCIUM(WT.%)=";A
150 PRINT "MAGNESIUM(WT.%)="B
160 PRINT "DOLOMITE(WT.%)=";C
170 PRINT "CALCITE(WT %)="F
180 PRINT "CO2 EQUIVALENT;S.T.P.(MLS/GM)=";G+H
190 GOTO 20
200 END
```

[3] 92.206 gm is GMW of dolomite; assuming Ca:Mg = 1:1 in dolomite

The print–out data from the recorder of the Atomic Absorption Spectro–photometer (i.e. – weight percentages of calcium and magnesium) are entered into the computer upon demand. The print–out from the computer is clear and concise, also the format is ideal for storage of results.

An example of a typical computer print–out is as follows:

Enter the sample name ?T–14
ENTER A (WT % CALCIUM)
?4.67
ENTER B (WT % MAGNESIUM)
?1.48
CALCIUM (WT.%)=4.67
MAGNESIUM(WT.%)=1.48
DOLOMITE (WT.%)=11.227
CALCITE (WT %)=5.56879
CO2 EQUIVAENT;(S.T.P.)(MLS/GM)=39.7374